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The Thermal Conductivity of Ethylene and Ethane

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The results of new, absolute measurements of the thermal conductivity of ethylene and ethane are reported. The measurements extend over the temperature range 308 to 425 K and for pressures up to 10 MPa and their accuracy is estimated to be ±0.3% under most conditions, although it deteriorates to ±2% at the lowest temperature and highest pressure near critical conditions. In the limit of zero density the data are employed to determine the diffusion coefficient for internal energy in the gases with the aid of independent measurements of other properties. It is found that vibrational energy transport must occur at a faster rate than diffusion of the molecules themselves, in contrast to the behavior usually observed for rotational energy. At elevated densities the concept of a temperature-independent excess thermal conductivity is found to fail at the highest level of accuracy owing to the proximity of the temperature range studied to the critical point. Nevertheless, the concept remains a useful predictive tool of modest accuracy.

KEY WORDS: Ethane; ethylene; high pressure; thermal conductivity; transport properties.

1. INTRODUCTION

As part of a series of accurate measurements of the density and temperature dependence of the thermal conductivity of gases, the present paper reports results for the two hydrocarbons ethane and ethylene. These two gases have considerable industrial significance and accurate data for their transport properties are therefore of interest. The two gases also provide

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examples of more complex molecular species than have been investigated hitherto [1–3] and, as such, are a more severe test of the available kinetic theory for the prediction of low-density properties and semiempirical estimation procedures for density effects.

2. EXPERIMENTAL

The thermal conductivity measurements for ethane and ethylene have been carried out in the transient hot-wire instrument described in detail elsewhere [1, 4–6]. The instrument was used unchanged for the present series of measurements, which extend over the temperature range 308 to 425 K for pressures up to 10 MPa. The usual experimental procedures have been adopted, and in particular, measurements of argon have been carried out to confirm the continued correct operation of the equipment by comparison with our earlier results [1]. The samples of ethane were supplied by Argo International with a stated purity of 99.99%, whereas the ethylene was supplied by British Oxygen Company with a purity of 99.92%. In the reduction of the experimental data the density and heat capacity of the gases have been taken from the equations of state of Bender [7, 8], which for ethylene in the range of interest here, yield values indistinguishable from a more recent equation [9].

In none of the measurements reported here was there any evidence of systematic departures of the behavior of the instrument from the theoretical model of it. In particular, no sign of degradation of the ethylene samples was observed [10]. However, at the lowest temperatures and highest pressures for both fluids, near their critical points, it was more difficult to retain a high precision owing principally to the high compressibility of the gas. For this reason it is estimated that while the accuracy of the thermal conductivity data is one of ±0.3% at moderate pressures for all temperatures, at the lowest temperature the uncertainty may be as much as ±2%.

3. RESULTS

Table I lists the thermal conductivity of argon remeasured along one isotherm (at 308.15 K) as a check on the operation of the instrument. Tables II to V list the data for ethylene along four isotherms (at 308.15, 333.15, 371.15, and 425.65 K) and Tables VI to IX the results for ethane along four isotherms (at 308.15, 331.65, 380.15, and 425.65 K). The data in each case are reported at nominal temperatures and the reference density [11]. The correction to the nominal temperatures has been accomplished by the application of a linear temperature correction which amounted to

Table I. The Thermal Conductivity of Argon at $T_{\text{nom}} = 308.15$ K

Pressure P (MPa)	Reference temperature T_r (°C)	Density at ref. temp. $\rho_r(T_r, P)$ (kg · m^{-3})	Thermal conductivity	
			$\lambda(T_r, \rho_r)$ (mW · m^{-1} · K^{-1})	$\lambda(T_{\text{nom}}, \rho_r)$ (mW · m^{-1} · K^{-1})
0.79	36.14	12.33	18.47	18.41
1.13	36.07	17.74	18.52	18.47
1.48	36.18	23.16	18.72	18.66
1.79	36.07	28.07	18.84	18.78
2.15	36.04	33.75	18.95	18.90
2.47	36.00	38.80	19.12	19.07
2.85	36.11	44.93	19.19	19.14
3.16	36.02	49.91	19.32	19.27
3.57	36.43	56.38	19.49	19.43
3.87	36.13	61.28	19.60	19.55
4.29	36.07	67.96	19.78	19.73
4.64	36.19	73.71	19.90	19.84
5.01	35.46	79.84	20.07	20.04
5.68	35.20	90.82	20.34	20.33
6.38	36.25	101.92	20.64	20.58
8.09	36.07	129.99	21.42	21.37
9.02	36.24	145.09	21.88	21.82

Table II. The Thermal Conductivity of Ethylene at $T_{\text{nom}} = 308.15$ K

Pressure P (MPa)	Reference temperature T_r (°C)	Density at ref. temp. $\rho_r(T_r, P)$ (kg · m^{-3})	Thermal conductivity	
			$\lambda(T_r, \rho_r)$ (mW · m^{-1} · K^{-1})	$\lambda(T_{\text{nom}}, \rho_r)$ (mW · m^{-1} · K^{-1})
0.51	34.95	5.71	22.77	22.78
0.85	35.07	9.77	22.86	22.85
1.25	35.08	14.69	23.19	23.18
1.57	35.08	18.77	23.34	23.33
1.98	35.01	24.26	23.60	23.60
2.29	35.04	28.65	24.05	24.04
2.58	35.07	32.93	24.47	24.46
2.94	35.08	38.62	24.98	24.97
3.85	34.97	54.43	26.78	26.77
4.22	34.94	61.98	27.84	27.85
4.58	34.92	69.77	28.88	28.89
4.92	34.93	77.80	29.95	29.96
5.24	35.10	85.92	31.18	31.17
5.70	34.96	99.81	33.47	33.48
6.10	34.98	113.7	34.58	35.98
6.47	34.95	128.7	38.87	38.88
6.86	35.03	147.2	43.11	43.10
7.46	35.05	180.5	49.30	49.29
7.98	34.98	210.7	55.21	55.21
8.48	34.98	235.7	58.96	58.97
8.82	35.11	249.4	61.37	61.36

Table III. The Thermal Conductivity of Ethylene at $T_{\mathrm{nom}} = 333.15$ K

Pressure P (MPa)	Reference temperature T_{r} (°C)	Density at ref. temp. $\rho_{\mathrm{r}}(T_{\mathrm{r}}, P)$ $(\mathrm{kg \cdot m^{-3}})$	Thermal conductivity	
			$\lambda(T_{\mathrm{r}}, \rho_{\mathrm{r}})$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	$\lambda(T_{\mathrm{nom}}, \rho_{\mathrm{r}})$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
0.42	58.61	4.331	25.80	25.97
0.74	58.55	7.793	25.99	26.16
1.06	58.69	11.27	26.00	26.16
1.78	58.13	19.65	26.58	26.78
2.19	59.05	24.60	27.18	27.30
2.37	59.99	27.95	27.57	27.57
2.82	59.33	32.58	27.79	27.87
3.17	59.37	37.25	28.29	28.37
3.58	58.13	43.18	28.77	28.95
4.35	59.67	54.53	30.21	30.25
5.04	59.47	65.85	31.60	31.66
5.66	59.67	76.94	32.96	33.00
6.50	59.56	93.94	35.39	35.44
7.12	59.50	108.00	37.56	37.62
7.66	58.42	122.84	39.60	39.79
8.55	58.42	147.90	43.96	44.15

Table IV. The Thermal Conductivity of Ethylene at $T_{\mathrm{nom}} = 371.15$ K

Pressure P (MPa)	Reference temperature T_{r} (°C)	Density at ref. temp. $\rho_{\mathrm{r}}(T_{\mathrm{r}}, P)$ $(\mathrm{kg \cdot m^{-3}})$	Thermal conductivity	
			$\lambda(T_{\mathrm{r}}, \rho_{\mathrm{r}})$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	$\lambda(T_{\mathrm{nom}}, \rho_{\mathrm{r}})$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
0.84	97.47	7.894	31.96	32.02
1.12	97.58	10.55	31.96	32.01
1.40	97.77	13.31	32.15	32.19
1.76	97.65	16.90	32.37	32.41
2.12	97.72	20.56	32.32	32.35
3.88	97.87	39.71	33.81	33.83
4.36	97.64	45.40	34.30	34.35
4.84	98.30	51.00	35.14	35.11
4.89	97.62	51.83	35.08	35.13
5.36	97.89	57.62	35.72	35.73
5.80	97.84	63.22	36.31	36.64
6.22	99.16	68.33	37.22	37.07
6.38	99.13	70.45	37.62	37.47
6.69	99.15	74.74	38.49	38.34

Table V. The Thermal Conductivity of Ethylene at $T_{\mathrm{nom}} = 425.65$ K

Pressure P (MPa)	Reference temperature T_r (°C)	Density at ref. temp. $\rho_r(T_r, P)$ $(\mathrm{kg \cdot m^{-3}})$	Thermal conductivity	
			$\lambda(T_r, \rho_r)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	$\lambda(T_{\mathrm{nom}}, \rho_r)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
1.39	152.98	11.29	41.94	41.88
1.72	152.99	14.00	41.98	41.91
2.03	153.06	16.69	42.21	42.13
2.38	152.94	19.70	42.02	41.96
2.69	153.00	22.39	42.38	42.31
3.04	152.98	25.35	42.52	42.45
3.46	153.00	29.14	42.61	42.54
3.77	153.26	31.90	42.52	42.42
4.16	152.83	35.44	43.13	43.09
4.51	152.82	38.68	43.16	43.12
4.97	152.79	42.98	43.61	43.54
5.42	152.81	47.21	43.78	43.74
5.79	152.80	50.76	44.01	43.97
6.14	152.90	54.14	44.43	44.37
6.49	152.71	57.53	44.62	44.60
6.73	152.90	59.86	45.19	45.13
7.00	152.79	62.54	45.18	45.14
7.60	152.84	68.59	45.82	45.77

Table VI. The Thermal Conductivity of Ethane at $T_{\mathrm{nom}} = 308.15$ K

Pressure P (MPa)	Reference temperature T_r (°C)	Density at ref. temp. $\rho_r(T_r, P)$ $(\mathrm{kg \cdot m^{-3}})$	Thermal conductivity	
			$\lambda(T_r, \rho_r)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	$\lambda(T_{\mathrm{nom}}, \rho_r)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
0.62	34.56	7.60	23.27	23.34
0.71	34.54	8.81	23.46	23.52
0.82	34.65	10.22	23.40	23.45
0.95	34.58	11.98	23.55	23.60
1.08	35.01	13.76	23.75	23.75
1.22	34.44	15.73	23.85	23.93
1.36	34.50	17.72	23.95	24.02
1.53	34.48	20.23	24.16	24.23
1.70	34.35	22.95	24.28	24.37
1.87	34.48	25.57	24.55	24.62
2.00	34.47	27.85	24.87	24.94
2.14	34.49	30.19	24.98	25.06
2.30	34.47	32.92	25.32	25.39
3.23	34.49	52.16	27.25	27.32
3.33	34.60	54.47	27.56	27.62
3.61	34.52	61.91	28.67	28.74
3.67	34.45	63.84	28.89	28.97
3.77	34.37	66.80	29.34	29.43
3.90	34.39	71.11	30.00	30.08

Table VII. The Thermal Conductivity of Ethane at $T_{\mathrm{nom}} = 331.65$ K

Pressure	Reference temperature	Density at ref. temp.	Thermal conductivity	
P (MPa)	T_r (°C)	$\rho_r(T_r, P)$ $(\mathrm{kg \cdot m^{-3}})$	$\lambda(T_r, \rho_r)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$	$\lambda(T_{\mathrm{nom}}, \rho_r)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
0.66	58.35	7.478	26.59	26.61
0.87	58.41	10.03	26.61	26.62
1.12	58.46	13.68	27.05	27.05
1.48	58.54	17.65	27.21	27.21
2.16	58.65	26.93	28.11	28.09
2.47	58.63	31.63	28.52	28.51
2.84	58.64	37.39	28.94	28.92
3.25	58.33	44.26	29.88	29.91
3.55	58.38	49.72	30.48	30.50
4.01	58.65	58.65	31.75	31.73
4.30	58.62	64.83	32.40	32.39
4.82	58.40	77.46	34.58	34.60
5.69	58.78	102.8	39.20	39.16
6.31	58.77	128.0	44.01	43.97

Table VIII. The Thermal Conductivity of Ethane at $T_{\mathrm{nom}} = 380.15$ K

Pressure	Reference temperature	Density at ref. temp.	Thermal conductivity	
P (MPa)	T_r (°C)	$\rho_r(T_r, P)$ $(\mathrm{kg \cdot m^{-3}})$	$\lambda(T_r, \rho_r)$ $(\mathrm{mW \cdot m^{-1}} \cdot K^{-1})$	$\lambda(T_{\mathrm{nom}}, \rho_r)$ $(\mathrm{mW \cdot m^{-1} \cdot K^{-1}})$
0.54	106.96	5.27	34.22	34.22
0.72	106.86	7.06	34.45	34.47
0.94	106.34	9.30	34.46	34.56
1.16	106.82	11.49	34.60	34.62
1.36	106.84	13.66	34.66	34.68
1.62	106.94	16.37	34.85	34.86
1.88	106.56	19.24	35.11	35.18
1.91	106.87	19.60	35.16	35.18
2.47	106.87	25.90	35.52	35.54
2.78	106.87	29.52	35.92	35.94
3.50	106.70	38.30	36.89	36.94
3.80	106.83	42.06	37.09	37.11
4.48	106.94	51.12	38.03	38.04
4.78	106.78	55.37	38.42	38.45

Table IX. The Thermal Conductivity of Ethane at $T_{\text{nom}} = 425.65$ K

Pressure P (MPa)	Reference temperature T_r (°C)	Density at ref. temp. $\rho_r(T_r, P)$ (kg·m^{-3})	Thermal conductivity $\lambda(T_r, \rho_r)$ (mW·m^{-1}·K^{-1})	Thermal conductivity $\lambda(T_{\text{nom}}, \rho_r)$ (mW·m^{-1}·K^{-1})
0.65	152.63	5.63	42.32	42.30
0.98	152.48	8.57	42.48	42.48
1.34	152.48	11.80	42.43	42.44
1.67	152.43	14.83	42.53	42.54
2.05	152.44	18.30	42.73	42.74
2.35	152.41	21.18	42.90	42.91
2.76	152.44	25.10	43.30	43.31
3.49	152.47	32.36	43.99	43.99
3.78	152.52	35.37	44.12	44.12
4.24	152.43	40.09	44.74	44.75
4.60	152.51	43.87	44.79	44.79
4.82	152.54	46.23	45.26	45.25
5.62	152.81	54.95	45.93	45.89
6.16	152.77	61.03	46.55	46.51
6.25	152.68	62.15	46.52	46.49
6.64	152.73	66.69	47.18	47.15
6.64	152.73	66.69	47.30	47.26

no more than ±0.4% in the thermal conductivity. The additional error contributed to the reported value of the thermal conductivity by this procedure is negligible.

It is estimated that for argon the uncertainty in the thermal conductivity is one of ±0.3% over the entire range of states studied. This is also the estimated error in the thermal conductivity of ethane and ethylene over most of the range studied. However, at the highest pressures and lowest temperature, the uncertainty is larger, amounting to ±2% owing to the proximity to the critical state.

For the purposes of interpolation and comparison, the experimental data for each gas along each isotherm have been represented by means of a finite polynomial in density of the form

$$\lambda = \sum_{i=0}^{n} c_i \rho^i \tag{1}$$

The coefficients, c_i, that secure the optimum representation of the data are listed in Table X. It is useful to note here, for future reference, that the higher-order coefficients for ethane and ethylene are significantly larger than those for argon. Although the coefficients derived by simple regression

Table X. Coefficients of the Correlation of the Thermal Conductivity of Eq. (1)

T (K)	c_0 ($\mathrm{mW} \cdot m^{-1} \cdot \mathrm{K}^{-1}$)	c_1 ($\mu\mathrm{W} \cdot \mathrm{m}^2 \cdot \mathrm{kg}^{-1} \cdot \mathrm{K}^{-1}$)	c_2 ($\mathrm{nW} \cdot \mathrm{m}^5 \cdot \mathrm{kg}^{-2} \cdot \mathrm{K}^{-1}$)	c_3 ($\mathrm{pW} \cdot \mathrm{m}^8 \cdot \mathrm{kg}^{-3} \cdot \mathrm{K}^{-1}$)
		Argon		
308.15	18.10	23.6	−6.0	136.0
		Ethylene		
308.15	22.61	19.3	1,162.0	−2,478.0
333.15	25.67	46.8	749.0	−1,507.0
371.15	31.76	21.42	684.9	2,438.0
425.65	41.82	−7.52	1,213.0	−3,765.0
		Ethane		
308.15	22.87	58.4	418.0	2,618.0
331.65	26.27	36.2	1,095.0	−2,305.0
380.15	34.18	16.8	1,937.0	−15,310.0
425.65	42.23	−0.99	2,075.0	−14,801.0

in this way have little physical significance, this observation indicates that the determination of the lower-order coefficients by statistical analysis of the data is significantly more difficult for the hydrocarbons than for argon.

For the check measurements of argon, Fig. 1 compares the present correlation with the results of an earlier series of measurements [1]. The maximum deviation amounts to no more than 0.67%, which is consistent with the combined, estimated accuracy of the two sets of data. The systematic nature of the deviations is a consequence of the fact that the precision of the measurements is inevitably better than their accuracy.

Figures 2 and 3 contain plots of the deviations of the results of the present measurements from the correlation of Eq. (1) with the coefficients in Table X. In addition, the same figures include the deviations of a selection of earlier measurements [10, 12–16] from the correlations. The departure of the present measurements from the correlation does not exceed ±0.6% for either gas and the standard deviation of the fit to the entire body of data is ±0.3%, which is consistent with the estimated precision.

The comparison of the present correlations with earlier results is somewhat difficult for these two systems, particularly at the lowest temperature and elevated densities, because the proximity to the critical point means that the temperature derivative of the thermal conductivity is strongly temperature and density dependent. Furthermore, there is no

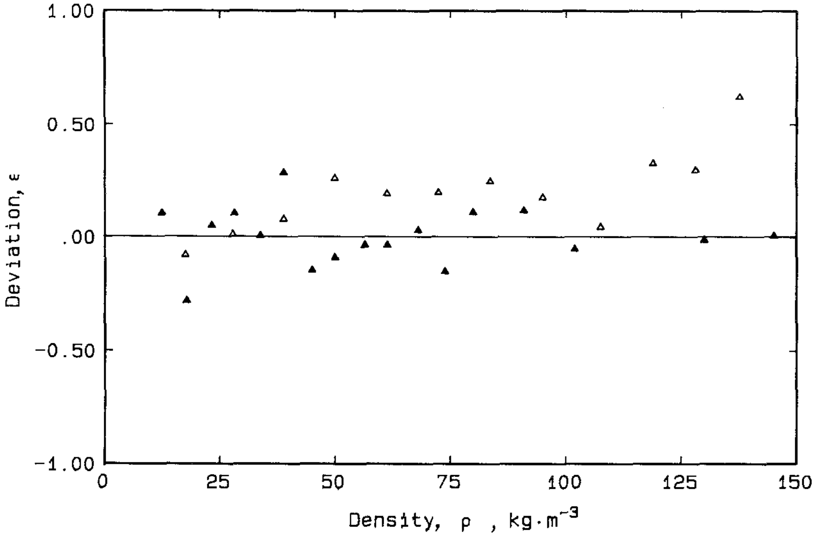

Fig. 1. The deviations of check measurements of the thermal conductivity of argon at 308.15 K from the correlation of Eq. (1). (▲) This work; (△) Ref. 1. $\varepsilon = [(\lambda_{\text{expt}} - \lambda_{\text{corr}})/\lambda_{\text{corr}}] \times 100\%$.

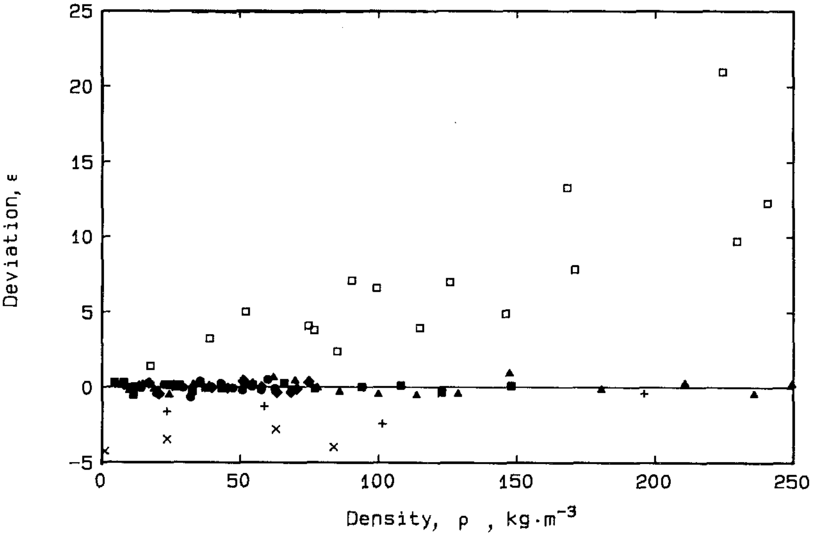

Fig. 2. Deviations of measurements of the thermal conductivity of ethylene from the present correlation. $\varepsilon = [(\lambda_{\text{expt}} - \lambda_{\text{corr}})/\lambda_{\text{corr}}] \times 100\%$. This work: (▲) 308.15 K; (■) 333.15 K; (◆) 371.15 K; (●) 425.65 K. Lenoir and Comings [12]: (+) 314.2 K; (x) 340.3 K. Prasad and Venart [10]: (□) 299 K.

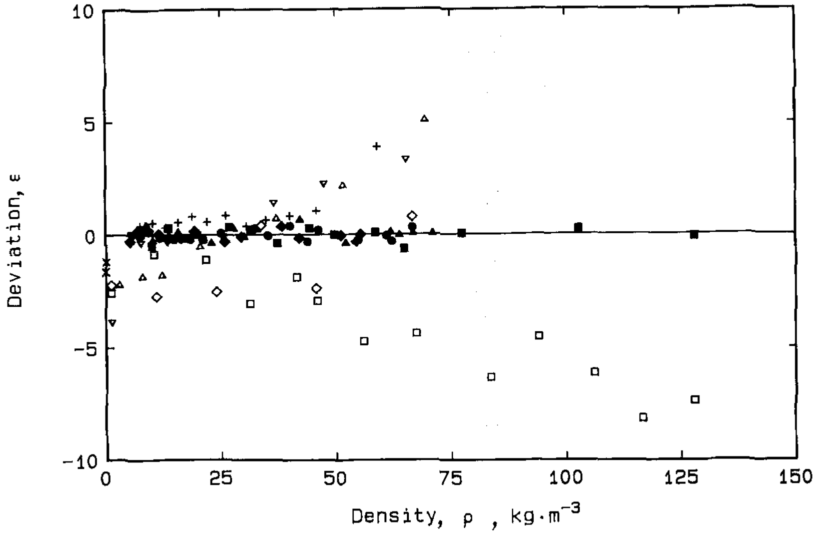

Fig. 3. Deviations of measurements of the thermal conductivity of ethane from the present correlation. $\varepsilon = [(\lambda_{\text{expt}} - \lambda_{\text{corr}})/\lambda_{\text{corr}}] \times 100\%$. This work: (▲) 308.15 K; (■) 331.65 K; (◆) 380.15 K; (●) 425.65 K. Roder [17]: (△) 305 K; (▽) 312 K. Tufeu *et al.* [16]: (x) 312 K. Lenoir *et al.* [15]: (□) 329.8 K; (◇) 315 K. Fleeter *et al.* [14]: (+) 300.6 K.

representative equation for $\lambda(\rho, T)$ which is as accurate as the present measurements [17]. For these reasons, the comparisons contained in Figs. 2 and 3 are somewhat crude because estimates of $(\partial\lambda/\partial T)_\rho$ have been used to adjust the data of other workers from their experimental temperatures to those employed here. In some cases the temperature correction amounts to a 10% change in the reported thermal conductivity and cannot be made with great certainty.

Figure 2 shows that the measurements of Prasad and Venart [10], the most extensive and recent for ethylene, are significantly higher at all densities than those reported here. The deviations increase to as much as 20% at the highest densities but even at the low densities, where the correction from one isotherm to another is most secure, the deviations are of the order of 3%. The earlier results of Lenoir and Comings [12] are, in contrast, significantly lower than the present data at both 308 and 333 K by as much as 5%. In view of the higher accuracy of the present data they are to be preferred in their range of thermodynamic states, although of course, they do not encompass the critical region.

For ethane, there have been a number of independent measurements of the thermal conductivity by a variety of techniques. Fleeter *et al.* [14]

and Roder [13, 17] employed a transient hot-wire technique and obtained results at 300.65 and at 305 and 312 K, respectively. These data have been approximately corrected to the present isotherm at 308 K and the deviations are shown in Fig. 3. At low densities, where the temperature correction is most accurate, the agreement with the results of Fleeter *et al.* [14] is good and within the mutual uncertainty of the two sets of data. At higher densities the discrepancies are larger and positive, probably as a result of an inadequate temperature correction. Similar comments apply to the data of Roder [13, 17], although the deviations from the latter, slightly less accurate, data are somewhat larger. The measurements of Tufeu *et al.* [16] in the limit of zero density lie about 1.5% below the present results, which may be interpreted as satisfactory agreement. Finally, the results of Lenoir *et al.* [15] fall up to 8% below the present correlation, almost certainly because of undetected errors in the earlier measurements.

3.1. Statistical Analysis

The correlation of Eq. (1) is intended merely as an interpolation scheme for the experimental data so that the coefficients in Table X cannot be ascribed a physical significance. However, by a careful statistical analysis of the density dependence of the thermal conductivity [18], it is possible to derive values for the first two coefficients in the density expansion of the thermal conductivity

$$\lambda = \lambda_0 + \lambda_1 \rho + \lambda_2 \rho^2 + \cdots \tag{2}$$

Table XI. The Derived Density Coefficients of Thermal Conductivity for Ethylene and Ethane

T (K)	λ_0 ($\mathrm{mW \cdot m^{-1} \cdot K^{-1}}$)	λ_1 ($\mathrm{\mu W \cdot m^2 \cdot kg^{-1} \cdot K^{-1}}$)
	Ethylene	
308.15	22.59 ± 0.12	20.8 ± 4.1
333.15	25.93 ± 0.18	4.6 ± 18
371.15	31.78 ± 0.18	16.6 ± 5.4
425.65	41.67 ± 0.25	8.1 ± 9.0
	Ethane	
308.15	22.87 ± 0.14	55.5 ± 6.5
331.65	26.14 ± 0.15	50.6 ± 3.2
380.15	34.01 ± 0.18	46.0 ± 7.7
425.65	42.29 ± 0.25	-3.8 ± 14

The methodology for extracting these coefficients has been described in detail elsewhere [18] so that here it is necessary merely to record that, as noted earlier, the higher coefficients in the density expansion for ethane and ethylene are large, and the coefficient λ_1 is small. In consequence, the uncertainty in the derived values of λ_0 and λ_1 is somewhat greater than that characteristic of the monatomic gases for example. The derived values of λ_0 and λ_1 for both ethylene and ethane are listed in Table XI together with their estimated uncertainties. In the case of λ_0 this estimate not only accounts for the statistical error in the quantity, but also for the accuracy of the absolute thermal conductivity measurements. Typically, the overall uncertainty in the tabulated λ_0 amounts to $\pm 0.5\%$. The first density coefficient of thermal conductivity for ethylene is particularly small and the value of zero is occasionally included within the rather large uncertainty band.

4. DISCUSSION

4.1. The Density Dependence of the Thermal Conductivity

The idea that the excess thermal conductivity of a gas

$$\Delta\lambda = \lambda(\rho, T) - \lambda_0(T) \tag{3}$$

is simply a function of density has been found to be supported by accurate experimental data for a number of gases far removed from their critical

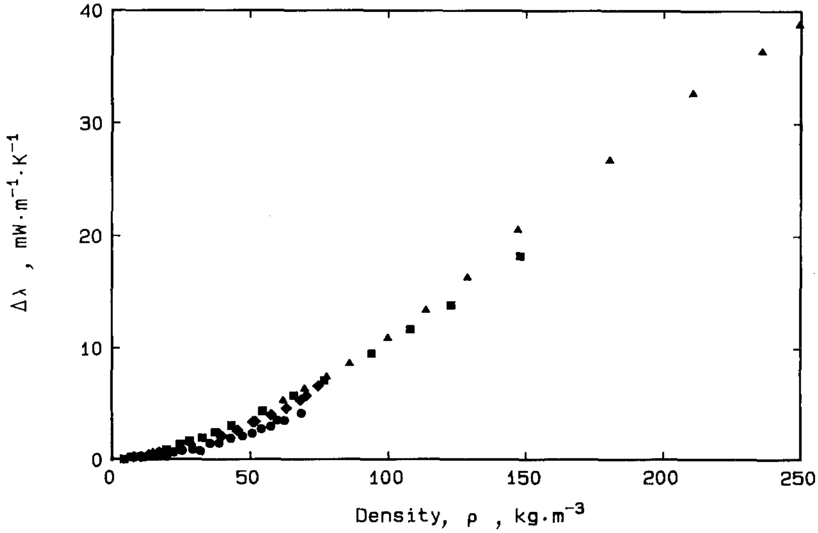

Fig. 4. The excess thermal conductivity of ethylene. (▲) 308.15 K; (■) 333.15 K; (◆) 371.15 K; (●) 425.65 K.

points [2]. Because this concept provides a powerful predictive tool for the thermal conductivity of fluids, it is worthwhile examining its validity with the aid of the present data for ethylene and ethane. The results of this examination are plotted in Figs. 4 and 5, which show the excess thermal conductivity plotted as a function of density for ethylene and ethane, respectively. For both gases there is a noticeable tendency for the excess property to decrease with increasing temperatures so that there is some temperature dependence in $\Delta\lambda$, although it is small. The source of this temperature dependence most probably lies in the critical enhancement of the thermal conductivity of both of these fluids [19]. However, a complete description of the behavior of the fluid in the neighborhood of the critical point requires an independent determination of the background and critical enhancement terms [20]. Such an analysis is beyond the scope of this paper, although the results contained here will clearly contribute to it subsequently.

One particular element of the density dependence of the thermal conductivity of gases is of special interest, namely, the first density coefficient, λ_1. In our earlier study [21] it was suggested that for monatomic and polyatomic gases a suitably defined, reduced first-density coefficient of thermal conductivity, defined by

$$\lambda_1^* = \frac{M(\lambda_1/\lambda_{\mathrm{tr,o}})}{[\frac{2}{3}\pi N_A \sigma_c^3]} + 0.625\left(\frac{\lambda_0}{\lambda_{\mathrm{tr,o}}} - 1\right) \tag{4}$$

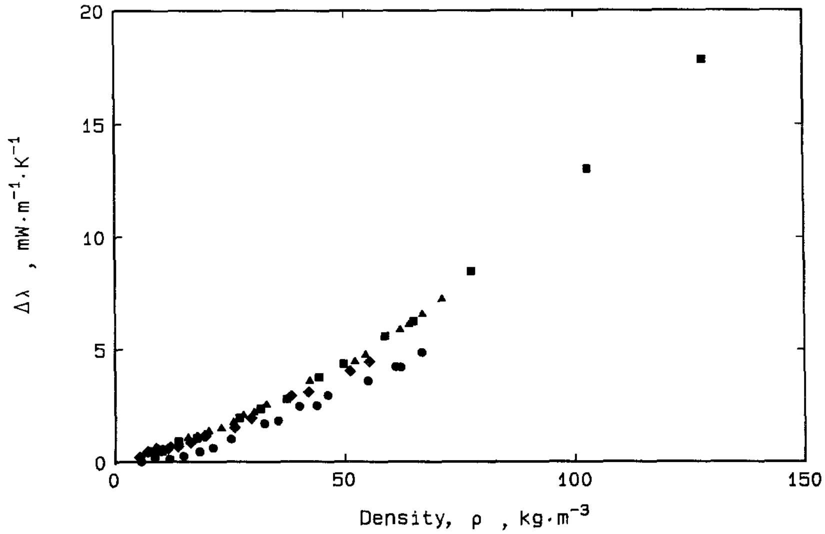

Fig. 5. The excess thermal conductivity of ethane. (▲) 308.15 K; (■) 331.65 K; (◆) 380.15 K; (●) 425.65 K.

could be represented by a universal function of the reduced temperature $T^* = kT/\varepsilon_c$. Here, N_A is Avagadro's constant, M is the molar mass of the gas, σ_c and ε_c are scaling parameters for length and energy, respectively [22, 23], and $\lambda_{tr,o}$ is an approximate value of the translational part of the zero-density thermal conductivity obtained by means of the relation [23]

$$\lambda_{tr,o} = \frac{15}{4}\frac{R}{M}\eta_0 \tag{5}$$

A correlation of available results for the thermal conductivity of monatomic gases yielded

$$\lambda_1^* = 0.323 + \frac{1.638}{T^*} + \frac{0.563}{T^{*2}} \quad \text{for} \quad 1.2 < T^* < 40 \tag{6}$$

The same function has been found to represent the behavior of $\lambda_1(T)$ for a number of [1, 3], but not for all [24], other polyatomic gases. Figure 6 displays the values of λ_1^* for ethylene and ethane for the present data, as well as those derived from the results of Fleeter *et al.* [14], together with the function of Eq. (6).

For neither gas does the function of Eq. (6) represent the temperature dependence of λ_1^* well. At low reduced temperatures for ethylene, the experimental values lie well below the correlation, whereas for ethane the

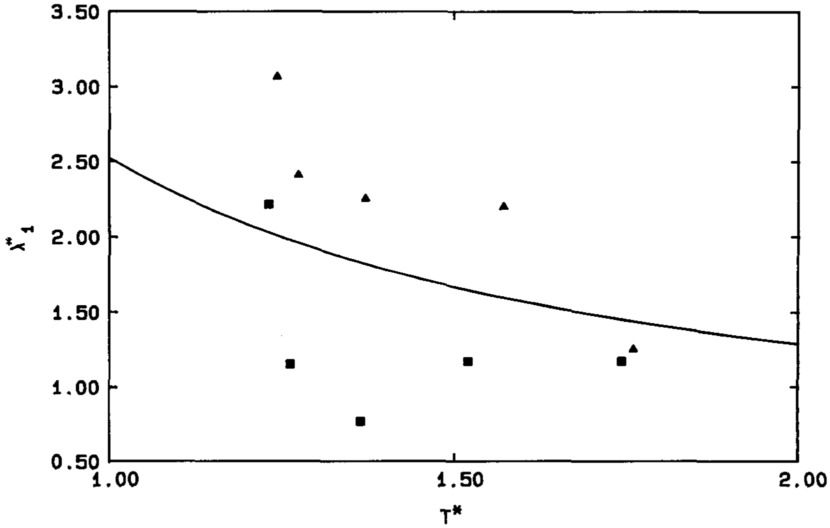

Fig. 6. Reduced first density coefficients for ethylene (■) and ethane (▲).

values are generally above those predicted by Eq. (6). At the highest temperature the experimental values for both gases are more nearly in agreement with the predictions of Eq. (6). The original formulation of Eq. (6) [21] relied on just one measurement for xenon for reduced temperatures around $T^* = 1.2$, so that the present results may be taken to imply a failure of the universality of λ_1^* defined by Eq. (4) at low reduced temperatures, which has already been suggested by results for tetrafluoromethane [3]. In turn, this suggests that a rather more rigorous theoretical treatment of energy transport in dense polyatomic gases, similar to that carried out by Rainwater and Friend [24] for monatomic species, is required before further progress can be made.

4.2. Zero Density

In the limit of zero density the theoretical framework for the interpretation of the present data is more secure than at elevated densities. In particular, within the Wang Chang and Uhlenbeck kinetic theory the thermal conductivity may be related to several effective cross sections, $\mathfrak{S}\left(\begin{smallmatrix} pqrs \\ pq'r's' \end{smallmatrix}\right)$, characteristic of molecular collisions in the gas. The result is [2]

$$\lambda_0 = \lambda_{\mathrm{tr}} + \lambda_{\mathrm{int}} \tag{7}$$

where

$$\lambda_{\mathrm{tr}} = \frac{5k^2T}{2m\langle v\rangle_0}\left[\frac{\mathfrak{S}(1001) + r\mathfrak{S}\left(\begin{smallmatrix} 1010 \\ 1001 \end{smallmatrix}\right)}{\mathfrak{S}(1010)\,\mathfrak{S}(1001) - \mathfrak{S}^2\left(\begin{smallmatrix} 1010 \\ 1001 \end{smallmatrix}\right)}\right] \tag{8}$$

and

$$\lambda_{\mathrm{int}} = \frac{5k^2T}{2m\langle v\rangle_0}\left[\frac{r\mathfrak{S}\left(\begin{smallmatrix} 1010 \\ 1001 \end{smallmatrix}\right) + r^2\mathfrak{S}(1010)}{\mathfrak{S}(1010)\,\mathfrak{S}(1001) - \mathfrak{S}^2\left(\begin{smallmatrix} 1010 \\ 1001 \end{smallmatrix}\right)}\right]\cdot S \tag{9}$$

with

$$\langle v\rangle_0 = 4(kT/\pi m)^{1/2} \tag{10}$$

$$r = (2c_{\mathrm{int}}/5k)^{1/2} \tag{11}$$

and

$$S = 1 - \frac{5}{3}\left(1 + \frac{\lambda_{\mathrm{tr}}}{\lambda_{\mathrm{int}}}\right)\left(\frac{\Delta\lambda_{\parallel}}{\lambda}\right)_{\mathrm{sat}} \tag{12}$$

Here, c_{int} is the internal heat capacity of the gas, m the molecular mass, and $(\Delta\lambda_{\parallel}/\lambda)_{\mathrm{sat}}$ the relative change in the thermal conductivity of the gas parallel to a magnetic field at saturation [23].

None of the effective cross sections $\mathfrak{S}\binom{p\,q\,r\,s}{p'q'r's'}$ can yet be evaluated exactly from an assumed intermolecular pair potential. However, it is known that some are more sensitive to the anisotropy of such pair potentials than others. Of particular interest are the combination $[\mathfrak{S}(1001)-\frac{1}{2}\mathfrak{S}(0001)]$, which enters in the so-called diffusion coefficient for internal energy [2],

$$D_{\text{int}}=\frac{kT}{nm\langle v\rangle_0}\left[\mathfrak{S}(1001)-\frac{1}{2}\mathfrak{S}(0001)\right]^{-1} \tag{13}$$

and $\mathfrak{S}(0001)$, which enters in the collision number for internal energy relaxation [2],

$$\zeta_{\text{coll}}=\frac{4kT}{\pi\eta_0\langle v\rangle_0\,\mathfrak{S}(0001)} \tag{14}$$

in which η_0 is the zero-density viscosity of the gas. The quantities D_{int} and ζ_{coll} are essential elements in either the representation or the prediction of the thermal conductivity of a dilute gas, and as yet, there is no exact or even approximate means of calculating them.

As we have shown earlier [2] the present experimental thermal conductivity data may be used, in conjunction with other experimental information, to derive values of the various effective cross sections. Ultimately, these effective cross sections may be of value in testing intermolecular pair potential functions, and in the interim, they can be employed in the formulation of schemes for the representation and calculation of the thermal conductivity based on sound physical theory [2, 20].

In the present analysis for ethylene and ethane we concentrate upon deriving values for the effective cross-section combination $[\mathfrak{S}(1001)-\frac{1}{2}\mathfrak{S}(0001)]$ or, more precisely, for the ratio of D_{int} to the self-diffusion coefficient of the gas D, where

$$D=\frac{kT}{nm\langle v\rangle_0}\left[\frac{1}{\mathfrak{S}(1000)}\right]$$

The ratio D_{int}/D is selected for study because there is some theoretical guidance about its asymptotic approach to unity at high temperatures for linear rigid rotors [2] and because it is a ratio which is unity in the case where inelastic collisions do not occur in the gas. It is therefore a measure of the extent to which inelastic collisions affect the thermal conductivity of the gas.

The methodology for the evaluation of D_{int}/D from experimental data has been described elsewhere. Here we need only to outline the procedure and the sources of information employed for ethylene and ethane.

First, we note that for both gases, both rotational and vibrational modes contribute substantially to the molecular energy and all the temperatures of interest here. Thus we must allow a different relaxation rate for the two modes of internal energy through the relation [25]

$$\frac{c_{\text{int}}}{\zeta_{\text{coll}}} = \frac{c_{\text{rot}}}{\zeta_{\text{rot}}} + \frac{c_{\text{vib}}}{\zeta_{\text{vib}}} \tag{15}$$

wherein the subscripts rot and vib stand for rotational and vibrational energy respectively.

4.2.1. Ethylene

For ethylene, ζ_{vib} has been determined over a range of temperatures by Corran *et al.* [26] and a representation of their results can be achieved with the correlation

$$\frac{1}{\zeta_{\text{vib}}} = 760.29 \times 10^{-4} \exp(-1264.8/T) \tag{16}$$

The collision number falls quite rapidly from approximately 1000 near room temperature to nearly 100 at 570 K. The internal contribution to the isochoric heat capacity, c_{int}, may be evaluated from the results of Jahangiri *et al.* [9] together with the two individual contributions to it. The viscosity of ethylene in the limit of zero density has been represented by Boushehri *et al.* [22] and we use their results unchanged.

The quantity $(\Delta\lambda_{\parallel}\lambda)_{\text{sat}}$ for ethylene has never been determined experimentally so that we are forced to assign it a value of zero. Judged by the results for other gases [1–3], it is unlikely that this assignment contributes more than 1 or 2% to the thermal conductivity and a sensitivity analysis indicates that the value selected does not materially affect our conclusions.

The final quantity required to permit evaluation of D_{int}/D is ζ_{rot} and this has been determined by Holmes *et al.* [27, 28], who quote a value between 1.3 and 2.0 collisions at 300 K. We have employed the value ζ_{rot} $(300\ \text{K}) = 1.4$ adopted earlier [14] together with the formula of Brau and Jonkman [29] for the temperature dependence of ζ_{rot} according to our previous analysis [2].

Table XII contains the values of D_{int}/D deduced from our experimental data, which indicate that the ratio is larger than unity at all temperatures and increases with increasing temperatures.

Table XII. The Ratio of the Diffusion Coefficient for Internal Energy to That for Mass, $[D_{\text{int}}/D]$

Ethylene T (K)	ζ_{rot}	D_{int}/D	Ethane T (K)	ζ_{rot}	D_{int}/D
308.15	1.42	1.022	308.15	1.43	0.998
333.15	1.53	1.037	331.65	1.54	1.014
371.15	1.69	1.074	380.15	1.75	1.061
425.65	1.92	1.143	425.65	1.94	1.100

4.2.2. Ethane

For ethane the internal energy relaxation process is more complicated since, in addition to the usual rotational and vibrational modes, ethane possesses a hindered rotation which contributes significantly to its heat capacity. This fact means that there is some confusion in the literature over the value of ζ_{vib}, which is variously quoted [28, 30, 31] as having values between 10 and 92 collisions near room temperature. A careful examination of the various sources indicates that this discrepancy arises from the occasional failure to distinguish the hindered rotational mode from other vibrational modes. For the present purposes, it is sufficient to use the value $\zeta_{\text{vib}} = 52$ at $T = 293$ K given by Lambert and Rowlinson [30], which represents the best estimate of the combined effect of the two models. In fact, we have used this value at all temperatures.

In the evaluation of D_{int}/D we have employed the heat-capacity data given by Younglove and Ely [32] to provide the separate contributions to c_{rot} and c_{vib}. The viscosity has been taken from the correlation of Boushehri *et al.* [22]. As for ethylene the spin-correction term $(\Delta\lambda_{\parallel}/\lambda)_{\text{sat}}$ is unknown so that we have assigned it the value zero, an assignment which, again, does not influence our major conclusions.

For ζ_{rot} there are no direct measurements, but based on earlier analyses [14] and the basic similarity of the ethane molecule with ethylene, the value $\zeta_{\text{rot}} = 1.4$ at $T = 300$ K seems reasonable. Again, we have employed the formula of Brau and Jonkman [29] to describe the temperature dependence of ζ_{rot}.

The derived values of D_{int}/D for ethane are listed in Table XII, and just as for ethylene, the values rise from near unity at 308 K to 1.10 at 425 K.

For linear rigid rotors it has been shown that D_{int}/D is asymptotic to unity from below as the temperature increases [2]. Although there is no proof, it is plausible to assume that the same pertains for the diffusion coefficient of rotational energy for other molecules. Furthermore, for systems in which inelastic collisions do not occur, $D_{\text{int}}/D = 1$. Consequently, the observation that for these two gases $D_{\text{int}} > 1$ implies that the transport of internal energy other than that associated with rotation must occur more rapidly than the transport of the molecules themselves as a result of inelastic collisions. Following Monchick *et al.* [25], when the internal energy of a molecule is contained in a number of modes, we must write

$$\frac{c_{\text{int}}}{(D_{\text{int}}/D)} = \frac{c_{\text{rot}}}{(D_{\text{rot}}/D)} + \frac{c_{\text{vib}}}{(D_{\text{vib}}/D)} \tag{17}$$

From this result we see that even if $D_{\text{rot}}/D = 1$, the value (D_{int}/D) depends upon the ratio (D_{vib}/D), provided that c_{vib} is significant. Thus, we conclude from the present study of ethane and ethylene that vibration energy transport must be more rapid than molecular energy transport. This is also consistent with our observations for methane [3] where $D_{\text{int}}/D > 1$ and for which vibrational energy is also significant. On the other hand, for molecules in which vibrational energy is less significant (e.g., nitrogen), it has been found that $D_{\text{int}}/D \leqslant 1$ [1, 2], which is consistent with the expected behavior of rotational energy transport alone.

5. CONCLUSIONS

On the basis of a kinetic theory analysis of the thermal conductivity data for ethylene and ethane at low density, it is concluded that vibrational energy transport is more rapid than the diffusion of the molecules themselves. Not only is this of interest from the point of view of molecular physics, where suitable intermolecular potential models must seek to explain the phenomenon, but also it is of considerable importance to the prediction of the thermal conductivity of gases because the neglect of such an effect can lead to errors in prediction of the order of 10%.

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